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Amines

Overview

- Amines are ammonia derivatives where 1, 2, or 3 H atoms are replaced by alkyl or aryl groups.
- Found naturally in proteins, vitamins, alkaloids, and hormones.

Solved Examples

- **Ex 1:** Identify the type of amine in CH_3NH_2.
  Answer: Primary amine (one alkyl group attached to N).

Practice Set

- Q1: What is an amine?
  A. A hydrocarbon
  B. Ammonia derivative
  C. Alcohol
  D. Ketone
- Q2: Amines are found in which natural compounds?
  A. Proteins
  B. Vitamins
  C. Alkaloids
  D. All of the above
- Q3: Which group replaces hydrogen in amines?
  A. Halogens
  B. Alkyl/Aryl groups
  C. Oxygen
  D. Sulfur

Answer Key

- Q1: B - Amines are derivatives of ammonia.

- Q2: D - Amines occur in proteins, vitamins, and alkaloids.
- Q3: B - Alkyl or aryl groups replace hydrogen atoms in amines.

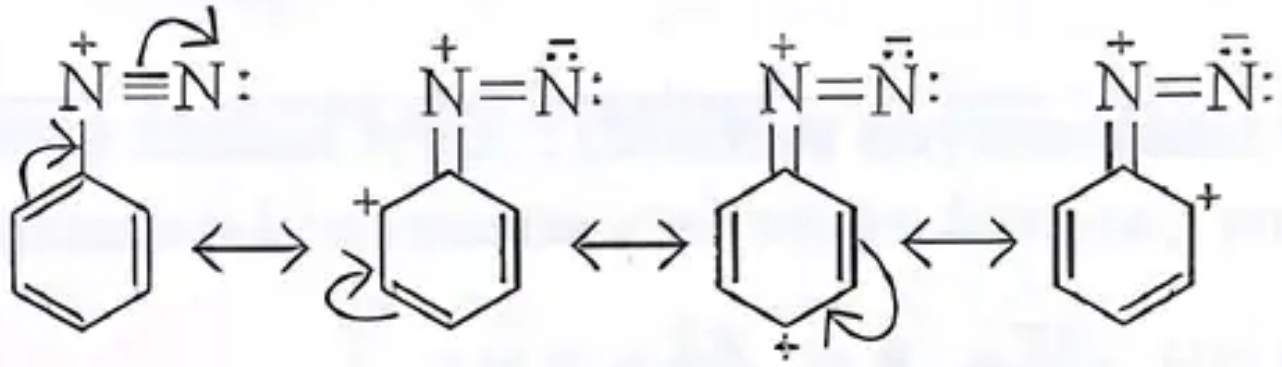
Memory Aids

- Amines = Ammonia + Alkyl/Aryl groups
- Natural occurrence: Proteins, Vitamins, Alkaloids

Diazonium Salts

Properties and Naming

- Arenediazonium salts have formula $ArN_2^+X^-$, where Ar = aryl group (e.g., C_6H_5), X = Cl^-, Br^-, NO_3^-, HSO_4^-, BF_4^-.
- Named by adding "diazonium" suffix to parent hydrocarbon + anion name (e.g., benzenediazonium chloride).
- Primary aliphatic amines form unstable alkyldiazonium salts.
- Primary aromatic amines form arenediazonium salts stable at 273-278 K.
- Arenediazonium salts are more stable due to positive charge delocalization over benzene ring.



Solved Examples

- **Ex 1:** Name $C_6H_5N_2^+Cl^-$.
  Answer: Benzenediazonium chloride.

Practice Set

- Q1: What is the general formula of arenediazonium salts?
  A. RNH_2
  B. $ArN_2^+X^-$
  C. RNO_2
  D. ArOH
- Q2: Which salt is more stable?
  A. Alkyldiazonium salt
  B. Arenediazonium salt
  C. Both equal
  D. None
- Q3: Benzenediazonium hydrogensulphate has formula:
  A. $C_6H_5N_2^+HSO_4^-$
  B. $C_6H_5NH_2$
  C. $C_6H_5NO_2$
  D. C_6H_5Cl

Answer Key

- Q1: B - Arenediazonium salts have formula $ArN_2^+X^-$.
- Q2: B - Arenediazonium salts are more stable due to resonance.
- Q3: A - Benzenediazonium hydrogensulphate is $C_6H_5N_2^+HSO_4^-$.

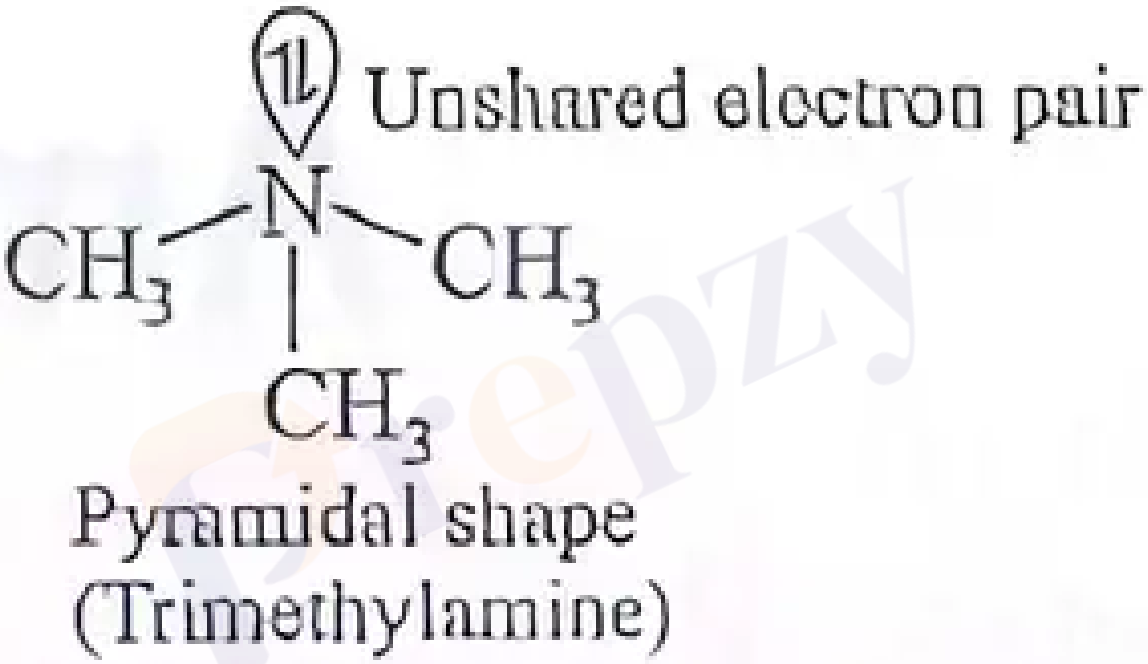
Memory Aids

- Diazonium salts: $ArN_2^+X^-$
- Stability: Arenediazonium > Alkyldiazonium
- Named by parent hydrocarbon + diazonium + anion

Structure of Amines

Geometry and Hybridization

- Nitrogen in amines is sp^3 hybridized.
- Amines have pyramidal shape due to lone pair on nitrogen.
- Bond angle C–N–E (E = C or H) is less than 109.5°, e.g., 108° in trimethylamine.



Solved Examples

- **Ex 1:** Describe the shape of trimethylamine.
  Answer: Pyramidal due to lone pair on N.

Practice Set

- Q1: What is the hybridization of nitrogen in amines?
  A. sp
  B. sp^2

C. sp^3

D. sp^3d

- Q2: What is the shape of amines?
  A. Linear
  B. Pyramidal
  C. Planar
  D. Tetrahedral
- Q3: Why is the bond angle in amines less than 109.5°?
  A. Lone pair repulsion
  B. Double bonds
  C. No lone pairs
  D. Hydrogen bonding

Answer Key

- Q1: C - Nitrogen is sp^3 hybridized in amines.
- Q2: B - Amines have pyramidal shape due to lone pair.
- Q3: A - Lone pair repulsion reduces bond angle below 109.5°.

Memory Aids

- Amines: sp^3 N, pyramidal shape
- Bond angle < 109.5° due to lone pair

Classification

Explanation

- Amines are classified based on the number of alkyl/aryl groups attached to the nitrogen atom.
- Primary amines (1°): One alkyl/aryl group attached to NH_2 (RNH_2).
- Secondary amines (2°): Two alkyl/aryl groups attached to NH (R_2NH).
- Tertiary amines (3°): Three alkyl/aryl groups attached to N (R_3N), no hydrogen on nitrogen.

- Examples:
  - Primary: Methanamine (CH_3-NH_2)
  - Secondary: N-Methyl methanamine (CH_3-NH-CH_3)
  - Tertiary: N,N-Dimethyl methanamine (CH_3-N(CH_3)-CH_3)

Primary amines : Amines containing $-NH_2$ group are called primary amines.

e.g., CH_3-NH_2, $C_6H_5-NH_2$,
Methanamine Benzenamine (aniline)

Secondary amines : Amines containing $-\overset{|}{N}H$ group are called secondary amines.

e.g., $CH_3-NH-CH_3$, $C_6H_5-NHCH_3$
N - Methyl methanamine *N* - Methyl aniline

Tertiary amines : Amines containing $-\overset{|}{\underset{|}{N}}$ group are called tertiary amines.

e.g., $H_3C-\underset{\underset{CH_3}{|}}{N}-CH_3$, $H_5C_6-\underset{\underset{CH_3}{|}}{N}-CH_3$
N,N-Dimethyl methanamine *N,N* - Dimethylaniline

Solved Examples

- **Ex 1:** Identify the type of amine: CH_3-NH_2.
  Solution: One alkyl group attached to NH_2 → Primary amine.
- **Ex 2:** Identify the type of amine: CH_3-NH-CH_3.
  Solution: Two alkyl groups attached to NH → Secondary amine.
- **Ex 3:** Identify the type of amine: CH_3-N(CH_3)-CH_3.
  Solution: Three alkyl groups attached to N, no H → Tertiary amine.

Practice Set

- **Q1:** Which of the following is a primary amine?
  A. CH_3-NH-CH_3
  B. CH_3-NH_2
  C. $N(CH_3)_3$
  D. NH_3
- **Q2:** Identify the secondary amine:
  A. CH_3-NH_2

B. CH_3-NH-CH_3
C. $N(CH_3)_3$
D. NH_3

- **Q3:** Which amine has no hydrogen attached to nitrogen?
  A. Primary amine
  B. Secondary amine
  C. Tertiary amine
  D. Ammonia

Answer Key

- **Q1:** B. CH_3-NH_2 - One alkyl group attached to NH_2 defines primary amine.
- **Q2:** B. CH_3-NH-CH_3 - Two alkyl groups attached to NH defines secondary amine.
- **Q3:** C. Tertiary amine - No hydrogen attached to nitrogen.

Memory Aids

- Primary amine = 1 alkyl group + NH_2.
- Secondary amine = 2 alkyl groups + NH.
- Tertiary amine = 3 alkyl groups, no H on N.
- Remember: "1° = 1 R, 2° = 2 R, 3° = 3 R" attached to N.

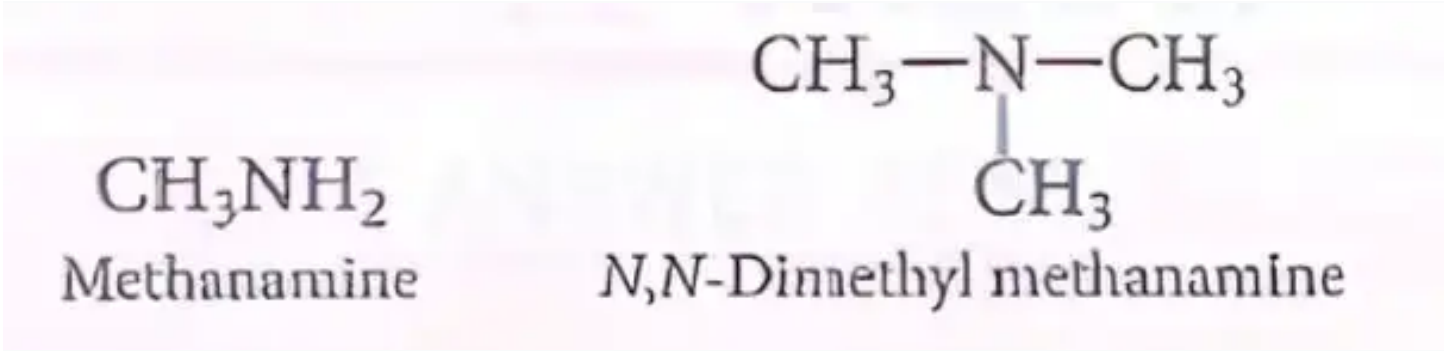
Nomenclature

Common System Naming

- Aliphatic amines named by prefixing alkyl group to "amine" (e.g., methylamine).

IUPAC System Naming

- Amines named as alkanamines.
- For secondary and tertiary amines, if alkyl groups are identical, use prefixes di-, tri- before alkyl name.



Solved Examples

- **Ex 1:** Name CH_3NH_2 - Methanamine (simple alkylamine).
- **Ex 2:** Name $(CH_3)_2NCH_3$ - N,N-Dimethyl methanamine (two methyl groups on N).

Practice Set

- **Q1:** What is the IUPAC name of CH_3NH_2?
  A. Methylamine
  B. Methanamine
  C. Ethylamine
  D. Methanamine N,N-dimethyl
- **Q2:** How is a tertiary amine with three identical alkyl groups named?
  A. Alkylamine
  B. Alkanamine
  C. Tri-alkylamine
  D. N,N-Dialkylamine
- **Q3:** What prefix is used when two identical alkyl groups are attached to nitrogen?
  A. Mono-
  B. Di-
  C. Tri-
  D. Tetra-

Answer Key

- **Q1:** B - Methanamine is the correct IUPAC name for CH_3NH_2.
- **Q2:** C - Tertiary amines with three identical alkyl groups use tri- prefix.
- **Q3:** B - Di- prefix is used for two identical alkyl groups on nitrogen.

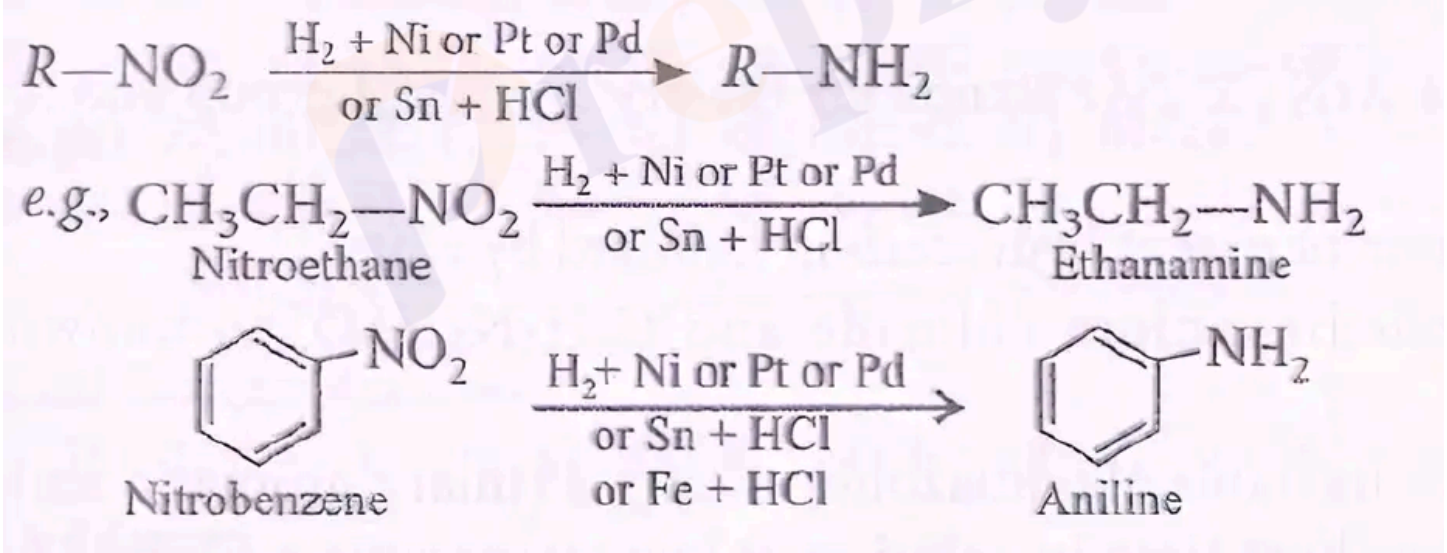
Memory Aids

- Common system: Alkyl + amine (e.g., methylamine).
- IUPAC: Alkanamine; use di-, tri- for multiple identical alkyl groups.
- Look for N-substitution to apply prefixes.

Preparation from Nitro Compounds

Explanation

- Nitro compounds (R–NO_2) are reduced to amines (R–NH_2).
- Reduction agents: H_2 with Ni, Pd, Pt catalysts or metals in acid (e.g., Sn + HCl).
- Commercially, iron scrap and HCl are used; FeCl formed hydrolyses to release HCl, requiring only a small amount of acid.
- Examples: Nitroethane → Ethanamine, Nitrobenzene → Aniline.



Solved Examples

- **Ex 1:** Reduce nitrobenzene using H_2/Pd catalyst → Aniline ($C_6H_5NH_2$).

Practice Set

- Q1: Which catalyst is NOT used for reduction of nitro compounds to amines?
  - A. Nickel
  - B. Palladium
  - C. Copper
  - D. Platinum
- Q2: What is the product of reduction of nitroethane?
  - A. Ethanolamine
  - B. Ethanamine
  - C. Ethylamine
  - D. Ethane
- Q3: Why is iron scrap used commercially with HCl in nitro compound reduction?
  - A. To increase temperature
  - B. To generate HCl in situ
  - C. To act as catalyst
  - D. To absorb hydrogen

Answer Key

- Q1: C - Copper is not used; Ni, Pd, Pt are common catalysts.
- Q2: B - Reduction of nitroethane gives ethanamine (primary amine).
- Q3: B - FeCl hydrolyses to release HCl, reducing the need for added acid.

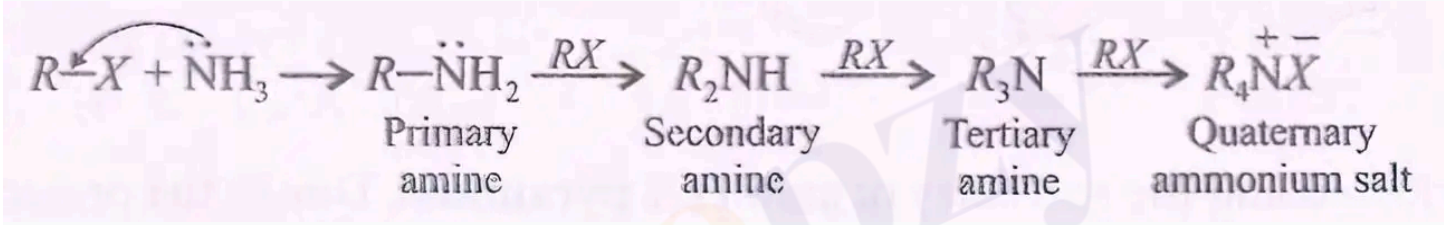
Memory Aids

- Reduction of $R–NO_2 \rightarrow R–NH_2$ using H_2/Ni, Pd, Pt or Sn/HCl.
- Iron scrap + HCl generates HCl in situ for commercial use.

Preparation from Alkyl Halides

Explanation

- Alkyl halides (R–X) react with ethanolic ammonia to give a mixture of primary, secondary, tertiary amines and quaternary ammonium salts.
- This process is called Hoffmann ammonolysis (cleavage of C–X bond by NH_3).
- Excess ammonia favors primary amine formation.
- Order of halide reactivity: R–I > R–Br > R–Cl.
- Reaction is nucleophilic substitution; ammonium salt formed is treated with strong base to get amine.
- Aryl halides do not undergo this reaction.
- Tertiary butyl bromide prefers elimination over substitution with NH_3.



Solved Examples

- **Ex 1:** React CH_3Br with excess NH_3 → CH_3NH_2 (primary amine).

Practice Set

- Q1: What is the main product when excess alkyl halide is used in Hoffmann ammonolysis?
  - A. Primary amine
  - B. Secondary amine
  - C. Tertiary amine
  - D. Quaternary ammonium salt
- Q2: Which halide reacts fastest in ammonolysis?
  - A. R–Cl
  - B. R–Br
  - C. R–I
  - D. Aryl halide
- Q3: What happens when tertiary butyl bromide reacts with NH_3?

- A. Substitution to amine
- B. Elimination
- C. No reaction
- D. Polymerization

Answer Key

- Q1: C - Excess alkyl halide gives mainly tertiary amine.
- Q2: C - R–I is most reactive.
- Q3: B - Tertiary butyl bromide undergoes elimination, not substitution.

Memory Aids

- Hoffmann ammonolysis: R–X + NH_3 → mixture of amines + quaternary salt.
- Excess NH_3 → primary amine; excess R–X → tertiary amine.
- Reactivity order: I > Br > Cl; aryl halides do not react.

Preparation from Nitriles

Explanation

- Nitriles (R–CN) are reduced to primary amines (R–CH_2NH_2).
- Reducing agents: $LiAlH_4$ or catalytic hydrogenation (H_2/Ni).
- Reduction by Na(Hg) and C_2H_5OH is called Mendius reduction.
- Example: CH_3Cl + KCN → CH_3CN (ethanenitrile), then reduced to ethylamine.

$$R-CN \xrightarrow[Na(Hg)\ /\ C_2H_5OH]{H_2/Ni} R-CH_2NH_2$$

This reaction is used for ascent of series *i.e.*, preparation of amines with more carbon atoms.

$$\underset{\text{Chloro-methane}}{CH_3Cl} \xrightarrow[\text{alcohol}]{KCN} \underset{\text{Ethanenitrile}}{CH_3-CN} \xrightarrow{\text{Reduction}} \underset{\text{Ethanamine}}{CH_3CH_2NH_2}$$

e.g.,

Solved Examples

- **Ex 1:** Reduce ethanenitrile with $LiAlH_4$ → Ethylamine.

Practice Set

- Q1: Which reagent is used for reduction of nitriles to primary amines?
  - A. $NaBH_4$
  - B. $LiAlH_4$
  - C. H_2SO_4
  - D. $KMnO_4$
- Q2: Mendius reduction involves reduction by:
  - A. Na(Hg) and C_2H_5OH
  - B. $LiAlH_4$
  - C. H_2/Ni
  - D. Sn and HCl
- Q3: What is the product when CH_3CN is reduced?
  - A. Methylamine
  - B. Ethylamine
  - C. Propylamine
  - D. Aniline

Answer Key

- Q1: B - $LiAlH_4$ is a strong reducing agent for nitriles.
- Q2: A - Mendius reduction uses Na(Hg) and ethanol.
- Q3: B - CH_3CN reduction gives ethylamine (2 carbon atoms).

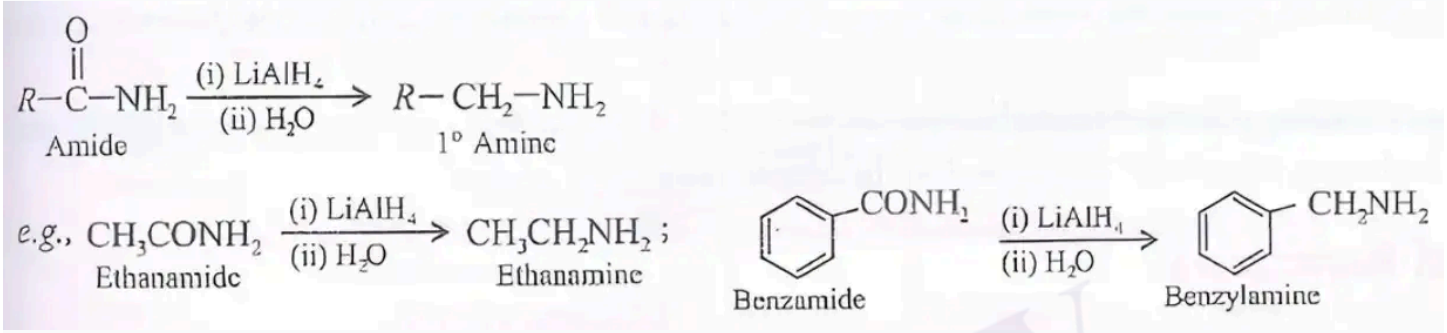
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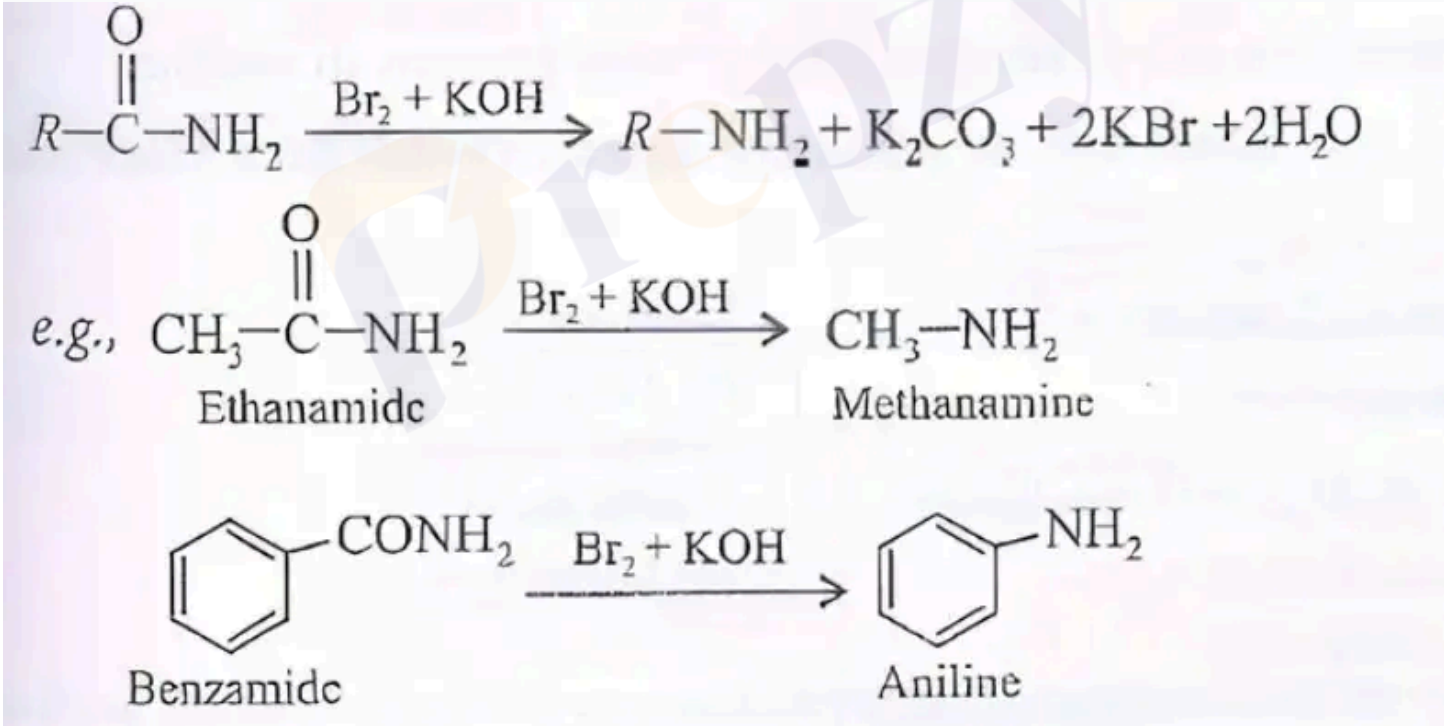
- Nitrile reduction adds two hydrogens to form primary amine.
- Mendius reduction = Na(Hg) + C_2H_5OH.

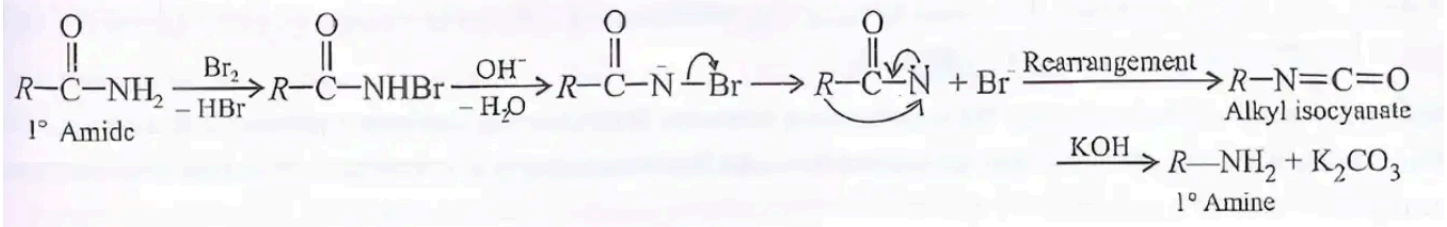
Preparation from Amides

Explanation

- Alkanamides (R-$CONH_2$) are reduced to primary amines using $LiAlH_4$.
- Hoffmann bromamide degradation: Primary amides treated with Br_2 and alkali give primary amines with one less carbon.
- Mechanism involves formation of bromoamide, isocyanate intermediate, then amine.







Solved Examples

- **Ex 1:** Reduce ethanamide with $LiAlH_4$ → Ethanamine.
- **Ex 2:** Treat benzamide with Br_2 and KOH → Aniline (one carbon less).

Practice Set

- Q1: What is the product of Hoffmann bromamide degradation?
  - A. Primary amine with same carbon number
  - B. Primary amine with one less carbon
  - C. Secondary amine
  - D. Tertiary amine
- Q2: Which reagent reduces amides to amines?
  - A. $NaBH_4$
  - B. $LiAlH_4$
  - C. H_2/Ni
  - D. Br_2/KOH
- Q3: What intermediate forms in Hoffmann bromamide degradation?
  - A. Isocyanate
  - B. Nitrile
  - C. Amide
  - D. Ammonium salt

Answer Key

- Q1: B - Primary amine with one less carbon is formed.
- Q2: B - $LiAlH_4$ reduces amides to amines.
- Q3: A - Isocyanate intermediate forms during reaction.

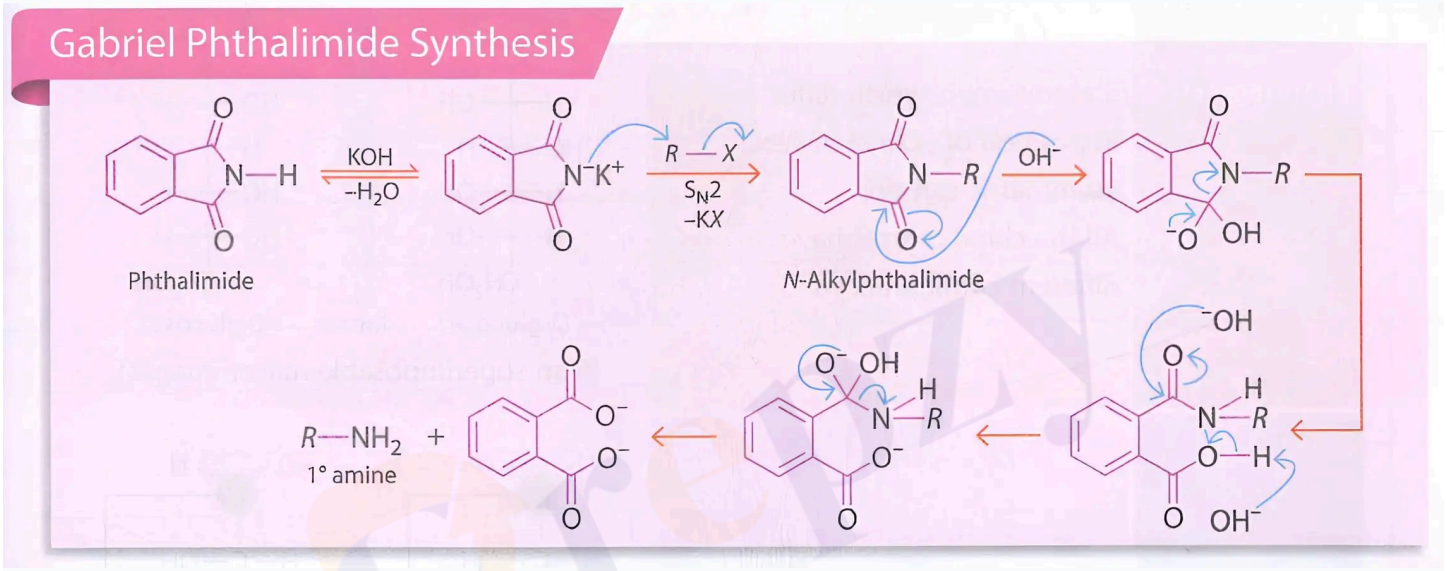
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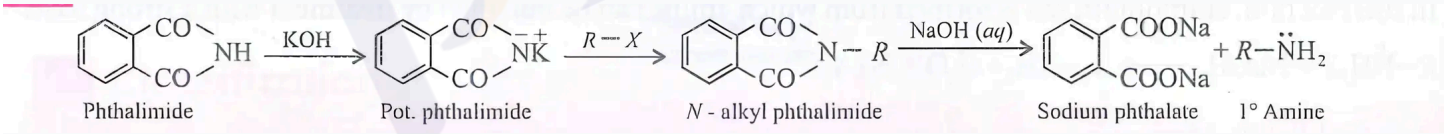
- Hoffmann bromamide degradation shortens carbon chain by one.
- $LiAlH_4$ reduces amides to primary amines.

Gabriel Phthalimide Synthesis

Explanation

- Potassium phthalimide reacts with alkyl halides to form N-alkyl phthalimide.
- Alkaline hydrolysis of N-alkyl phthalimide produces primary amines.
- Used to prepare primary amines without secondary/tertiary amines.
- 1° aromatic amines (aniline, toluidines) cannot be prepared as aryl halides do not react under mild conditions.





Solved Examples

- **Ex 1:** React potassium phthalimide with ethyl bromide → N-ethyl phthalimide, then hydrolyze → ethylamine.

Practice Set

- Q1: What is the main product of Gabriel synthesis?
  - A. Secondary amine
  - B. Tertiary amine
  - C. Primary amine

    - D. Quaternary ammonium salt
- Q2: Why can't aromatic amines be prepared by Gabriel synthesis?
    - A. Aryl halides do not undergo nucleophilic substitution
    - B. Reaction is too slow
    - C. Phthalimide is unstable
    - D. Aromatic amines are unstable
- Q3: Which reagent is used to hydrolyze N-alkyl phthalimide?
    - A. HCl
    - B. NaOH
    - C. KOH
    - D. NH_3

Answer Key

- Q1: C - Gabriel synthesis produces primary amines.
- Q2: A - Aryl halides do not undergo nucleophilic substitution under mild conditions.
- Q3: B - NaOH is used for hydrolysis.

Memory Aids

- Gabriel synthesis: potassium phthalimide + R–X → N-alkyl phthalimide → hydrolysis → primary amine.
- Does not work for aryl halides (no nucleophilic substitution).

Physical Properties

Physical State

- Lower aliphatic amines: gases with ammoniacal smell.
- Primary amines (≥3 C atoms): liquids with fishy odour.
- Lower aromatic amines: liquids with unpleasant odour.
- Higher aromatic amines: solids, odourless.

Colour

- Pure amines are colourless.
- Get coloured due to atmospheric oxidation.

Solubility

- Amines are soluble in water due to hydrogen bonding.
- Solubility decreases with increasing alkyl size.
- Higher and aromatic amines are insoluble in water but soluble in organic solvents.

Boiling Points

- Amines are polar and form intermolecular hydrogen bonds (except tertiary amines).
- Exist as associated molecules, showing higher boiling points than hydrocarbons of similar molecular mass.
- Boiling points are lower than alcohols and carboxylic acids of comparable molecular mass.
- Order of boiling points: 1° > 2° > 3° amines due to number of hydrogen atoms available for bonding.

Solved Examples

- **Ex 1:** Identify physical state of amine with 2 carbon atoms.
  Answer: Gas with ammoniacal smell (lower aliphatic amine).
- **Ex 2:** Compare boiling points of 1° and 3° amines.
  Answer: 1° amine has higher boiling point due to more hydrogen bonding.

Practice Set

- **Q1:** What is the physical state of primary amines with three or more carbon atoms?
  A. Gas
  B. Liquid
  C. Solid
  D. Colourless gas

- **Q2:** Why do pure amines get coloured on exposure to air?
  A. Reaction with water
  B. Atmospheric oxidation
  C. Hydrogen bonding
  D. Polymerization
- **Q3:** Which order correctly represents boiling points of isomeric amines?
  A. 3° > 2° > 1°
  B. 1° > 2° > 3°
  C. 2° > 1° > 3°
  D. 1° > 3° > 2°

Answer Key

- **Q1:** B - Primary amines with ≥3 carbons are liquids with fishy odour.
- **Q2:** B - Amines get coloured due to atmospheric oxidation.
- **Q3:** B - Boiling points decrease from 1° to 3° due to hydrogen bonding availability.

Memory Aids

- Lower aliphatic amines: gas + ammoniacal smell.
- Boiling point order: 1° (two H) > 2° (one H) > 3° (no H).
- Pure amines colourless; colour on air due to oxidation.

Chemical Reactions

Overview of Primary Amine Reactions

- Primary amines (RNH_2) undergo alkylation with alkyl halides (R'X) to form secondary, tertiary amines, and quaternary ammonium salts.
- Acylation with acid chlorides (R'COCl) or anhydrides forms amides (RNH-COR').
- Benzoylation with benzoyl chloride (C_6H_5COCl) produces benzamides ($RNHCOC_6H_5$).
- Carbylamine test: Primary amines react with chloroform and alcoholic KOH to form isocyanides (RNC), confirming primary amines.
- Hinsberg’s test: Primary amines react with benzenesulfonyl chloride to form soluble sulfonamides in alkali.

- Nitrous acid reaction: Primary amines react with HNO_2 to give alcohols, nitrogen gas, and water.

Solved Examples

- Ex 1: Alkylation of methylamine (CH_3NH_2) with ethyl bromide (C_2H_5Br) forms ethylmethylamine.
- Ex 2: Carbylamine test with an unknown amine producing foul-smelling isocyanide confirms primary amine.

Practice Set

- Q1: Which reagent is used in the carbylamine test?
  - A. Chloroform and alcoholic KOH
  - B. Benzoyl chloride
  - C. Nitrous acid
  - D. Alkyl halide
- Q2: Primary amines react with benzenesulfonyl chloride to form?
  - A. Insoluble sulfonamides
  - B. Soluble sulfonamides
  - C. Quaternary ammonium salts
  - D. Isocyanides
- Q3: Reaction of primary amines with nitrous acid produces?
  - A. Alcohols and nitrogen gas
  - B. N-nitrosamines
  - C. Nitrite salts
  - D. Diazonium salts

Answer Key

- Q1: A - Chloroform and alcoholic KOH produce isocyanides in carbylamine test.
- Q2: B - Primary amines form soluble sulfonamides with benzenesulfonyl chloride.
- Q3: A - Primary amines react with nitrous acid to give alcohols and nitrogen gas.

Memory Aids

- Carbylamine test positive only for primary amines.
- Hinsberg's test solubility distinguishes 1°, 2°, and 3° amines.
- Nitrous acid reaction: primary amines → alcohols; aromatic primary amines → diazonium salts.

Basic Character of Amines

Key Points on Basicity

- Amines are basic due to lone pair on nitrogen.
- Aliphatic amines are stronger bases than ammonia due to +I effect of alkyl groups.
- Basicity affected by inductive, steric, solvation, and resonance effects.
- Gaseous phase basicity order: 3° amine > 2° amine > 1° amine > NH_3.
- Aqueous phase basicity varies due to solvation; e.g., $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_3 > NH_3$.
- Aromatic amines are weaker bases due to resonance delocalization of lone pair.

Solved Examples

- Ex 1: Compare basicity of methylamine and aniline; methylamine is stronger base due to no resonance.
- Ex 2: Explain why 3° amines are more basic than 1° in aqueous phase due to steric hindrance reducing solvation.

Practice Set

- Q1: Why are aliphatic amines stronger bases than ammonia?
  - A. Resonance effect
  - B. +I effect of alkyl groups
  - C. Steric hindrance
  - D. Solvation effect
- Q2: Order of basicity in gaseous phase is?

    - A. 1° > 2° > 3° > NH_3
    - B. 3° > 2° > 1° > NH_3
    - C. NH_3 > 1° > 2° > 3°
    - D. 2° > 3° > 1° > NH_3
- Q3: Aromatic amines are weaker bases because?
    - A. Lone pair is localized on nitrogen
    - B. Lone pair is delocalized over benzene ring
    - C. They have no lone pair
    - D. They are sterically hindered

Answer Key

- Q1: B - +I effect of alkyl groups increases electron density on nitrogen.
- Q2: B - Gaseous phase basicity order is 3° > 2° > 1° > NH_3.
- Q3: B - Resonance delocalizes lone pair, reducing availability for protonation.

Memory Aids

- Basicity in aqueous phase affected by solvation and steric hindrance.
- Aromatic amines weaker bases due to resonance.
- 3° amines more basic than 1° in aqueous phase due to steric effects.

Distinction Between 1°, 2° and 3° Amines

Hinsberg's Test

- Primary amines react with benzenesulfonyl chloride to form N-alkylbenzenesulfonamides soluble in alkali.
- Secondary amines form N,N-dialkylbenzenesulfonamides insoluble in alkali.
- Tertiary amines do not react.

Solved Examples

- Ex 1: Identify amine type by solubility of Hinsberg’s test product in alkali.

Practice Set

- Q1: Hinsberg’s test product soluble in alkali indicates?
  - A. Primary amine
  - B. Secondary amine
  - C. Tertiary amine
  - D. Quaternary ammonium salt
- Q2: Which amine does not react with Hinsberg’s reagent?
  - A. Primary
  - B. Secondary
  - C. Tertiary
  - D. Quaternary
- Q3: Hinsberg’s test distinguishes amines based on?
  - A. Solubility of sulfonamide
  - B. Color change
  - C. Gas evolution
  - D. Precipitate formation

Answer Key

- Q1: A - Soluble sulfonamide indicates primary amine.
- Q2: C - Tertiary amines do not react with Hinsberg’s reagent.
- Q3: A - Test is based on solubility differences of sulfonamides.

Memory Aids

- Hinsberg’s test: Primary soluble, secondary insoluble, tertiary no reaction.
- Carbylamine test positive only for primary amines.
- Azo dye test positive only for primary aromatic amines.

Electrophilic Substitution Reactions of Arylamines

Key Reactions of Aniline

- Aniline undergoes electrophilic substitution; —NH_2 is ortho/para directing and activating.
- Bromination forms tribromoaniline or p-bromoaniline.
- Nitration forms p-nitroaniline.
- Sulfonation with H_2SO_4 forms sulphanilic acid (zwitter ion).
- Diazotization with $NaNO_2$/HCl forms diazonium salt.
- Reaction with chloroform and KOH forms phenyl isocyanide.
- Oxidation forms p-benzoquinone.
- Aniline forms salt with $AlCl_3$ during alkylation, deactivating electrophilic substitution; no Friedel-Crafts reaction.

Solved Examples

- Ex 1: Bromination of aniline yields tribromoaniline due to activating —NH_2 group.
- Ex 2: Explain why aniline does not undergo Friedel-Crafts alkylation.

Practice Set

- Q1: The —NH_2 group in aniline directs substitution to?
  - A. Meta position
  - B. Ortho and para positions
  - C. Only para position
  - D. No substitution
- Q2: Why does aniline not undergo Friedel-Crafts reaction?
  - A. It is too reactive
  - B. Forms salt with $AlCl_3$ deactivating ring
  - C. No lone pair on nitrogen
  - D. It is a weak base
- Q3: Diazonium salt formation requires?
  - A. $NaNO_2$ and HCl at 0-5 °C
  - B. Chloroform and KOH
  - C. Bromine water

- D. Concentrated H_2SO_4

Answer Key

- Q1: B - —NH_2 is ortho/para directing.
- Q2: B - Aniline forms salt with $AlCl_3$, deactivating electrophilic substitution.
- Q3: A - Diazotization requires $NaNO_2$ and HCl at low temperature.

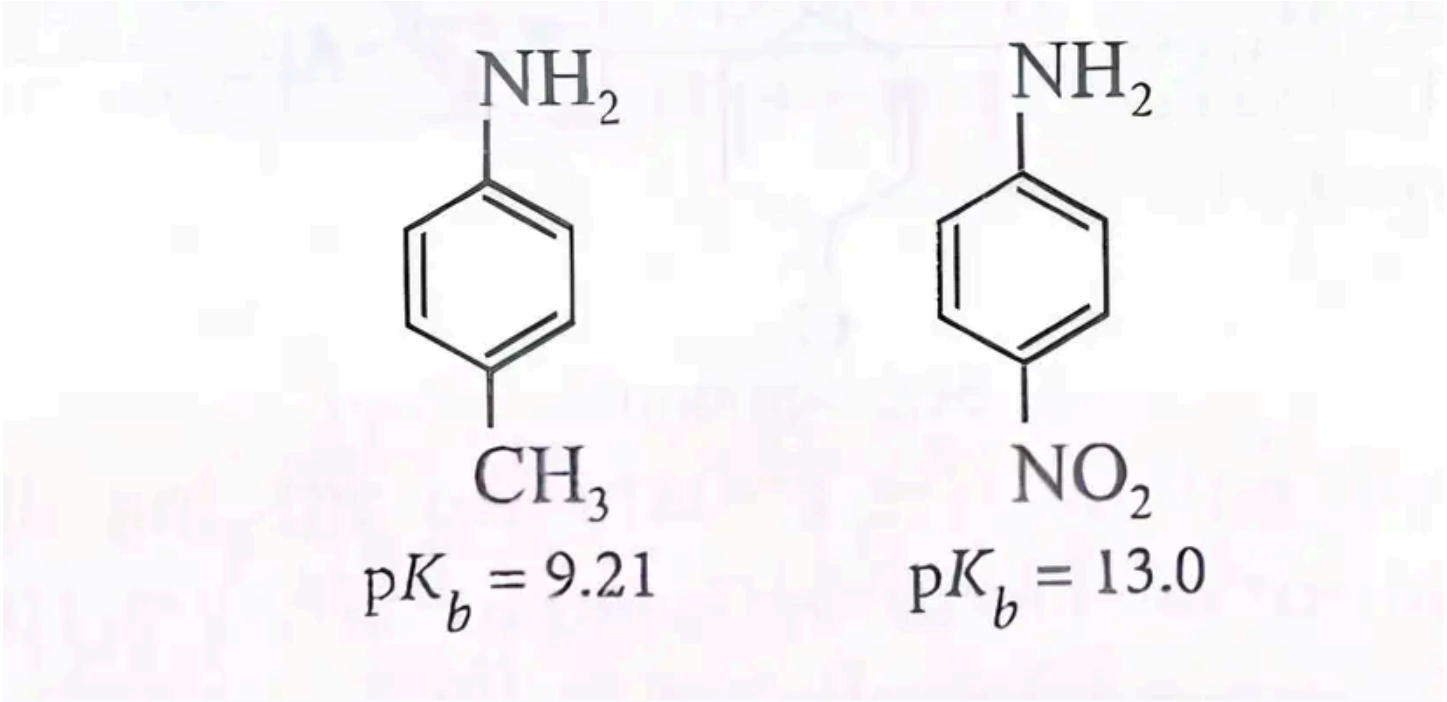
Memory Aids

- —NH_2 group activates and directs ortho/para substitution.
- Aniline salt formation with $AlCl_3$ prevents Friedel-Crafts reaction.
- Diazonium salts form at 0-5 °C with $NaNO_2$/HCl.

Basicity of Substituted Anilines

Effect of Substituents

- Electron releasing groups (-OCH_3, -CH_3) increase electron density on nitrogen, enhancing basicity.
- Electron withdrawing groups (-NO_2, -SO_3H, -COOH, -X) decrease basicity.
- pK_b values indicate strength: lower pK_b means stronger base.



Solved Examples

- Ex 1: Compare pK_b of p-methylaniline (9.21) and p-nitroaniline (13.0); methyl group increases basicity.

Practice Set

- Q1: Which group increases basicity of aniline?
  - A. $-NO_2$
  - B. $-SO_3H$
  - C. $-CH_3$
  - D. -COOH
- Q2: Lower pK_b value indicates?
  - A. Weaker base
  - B. Stronger base
  - C. No change
  - D. Acidic nature
- Q3: Electron withdrawing groups cause?
  - A. Increase in basicity
  - B. Decrease in basicity
  - C. No effect
  - D. Increase in acidity

Answer Key

- Q1: C - Electron donating -CH_3 increases basicity.
- Q2: B - Lower pK_b means stronger base.
- Q3: B - Electron withdrawing groups decrease basicity.

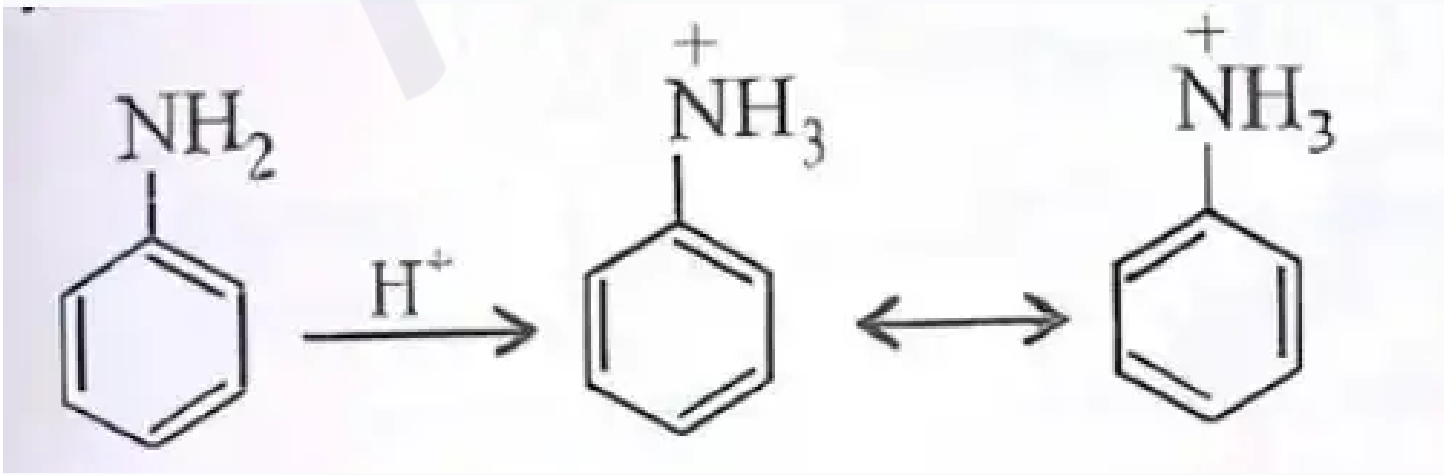
Memory Aids

- Electron donating groups increase basicity; withdrawing groups decrease it.
- pK_b values help compare basic strengths.

Anilinium Ion Stability

Key Points

- Anilinium ion (protonated aniline) has fewer resonance structures (2) than aniline (5), making it less stable.
- Protonation reduces electron delocalization on nitrogen.



Solved Examples

- Ex 1: Explain why anilinium ion is less stable than aniline based on resonance.

Practice Set

- Q1: Anilinium ion is less stable because?
  - A. More resonance structures
  - B. Fewer resonance structures
  - C. No lone pair on nitrogen
  - D. It is neutral
- Q2: Protonation affects aniline by?
  - A. Increasing electron delocalization
  - B. Decreasing resonance
  - C. No effect
  - D. Increasing basicity
- Q3: Resonance in aniline involves?
  - A. Benzene ring and nitrogen lone pair
  - B. Only benzene ring
  - C. Only nitrogen lone pair
  - D. No resonance

Answer Key

- Q1: B - Anilinium ion has fewer resonance forms, less stable.
- Q2: B - Protonation reduces resonance delocalization.
- Q3: A - Resonance involves benzene ring and nitrogen lone pair.

Memory Aids

- Protonation reduces resonance, lowering stability.
- Aniline has 5 resonance forms; anilinium ion has 2.

Method of Preparation of Diazonium Salts

Explanation

- Benzenediazonium chloride is prepared by reacting aniline ($C_6H_5NH_2$) with nitrous acid (HNO_2), generated in situ from sodium nitrite ($NaNO_2$) and hydrochloric acid (HCl).
- The reaction is carried out at low temperature (0-5 °C) to maintain the stability of the diazonium salt.
- This process is called diazotisation — conversion of primary aromatic amines into diazonium salts.
- Diazonium salts are unstable and generally used immediately after preparation.
- Chemical reaction:
  - $C_6H_5NH_2 + NaNO_2 + 2HCl \rightarrow C_6H_5N_2^+Cl^- + NaCl + 2H_2O$

$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{0\text{-}5\ ^\circ C} C_6H_5N_2^+Cl^- + NaCl + 2H_2O$$

Solved Examples

- **Ex 1:** Write the reaction for the preparation of benzenediazonium chloride from aniline.
  - React aniline with $NaNO_2$ and HCl at 0-5 °C.
  - Product formed: $C_6H_5N_2^+Cl^-$ (benzenediazonium chloride).

Practice Set

- **Q1:** What is the temperature range for the diazotisation reaction?
  - A. 25-30 °C
  - B. 0-5 °C
  - C. 50-60 °C
  - D. 10-15 °C
- **Q2:** Which reagent is NOT used in the preparation of benzenediazonium chloride?
  - A. Aniline
  - B. Sodium nitrite
  - C. Hydrochloric acid
  - D. Sulfuric acid

- **Q3:** What are the by-products formed during the diazotisation of aniline?
  - A. NaCl and H_2O
  - B. NaOH and H_2O
  - C. HCl and $NaNO_2$
  - D. NH_3 and HCl

Answer Key

- **Q1:** B. 0-5 °C — Low temperature is required to stabilize the diazonium salt.
- **Q2:** D. Sulfuric acid — HCl is used, not H_2SO_4.
- **Q3:** A. NaCl and H_2O — These are the by-products formed in the reaction.

Memory Aids

- Diazotisation = Primary aromatic amine + $NaNO_2$ + HCl at 0-5 °C → Diazonium salt.
- Keep temperature low to prevent decomposition.
- Diazonium salts are unstable; use immediately.

Physical Properties

Properties of Benzenediazonium Chloride

- Colourless crystalline solid.
- Readily soluble in water.
- Stable when kept cold.
- Reacts with water on warming.
- Decomposes easily in dry state.

Properties of Benzenediazonium Fluoroborate

- Insoluble in water.
- Stable at room temperature.

Solved Examples

- **Ex 1:** Identify the solubility of benzenediazonium chloride.
  - Answer: Soluble in water.
- **Ex 2:** State the stability condition of benzenediazonium fluoroborate.
  - Answer: Stable at room temperature.

Practice Set

- **Q1:** What is the physical state of benzenediazonium chloride?
  - A. Colourless crystalline solid
  - B. Coloured liquid
  - C. Powdered solid
  - D. Gaseous
- **Q2:** Which of the following is true about benzenediazonium chloride?
  - A. Insoluble in water
  - B. Stable when warm
  - C. Decomposes easily when dry
  - D. Stable at room temperature
- **Q3:** Benzenediazonium fluoroborate is:
  - A. Water soluble and unstable
  - B. Water insoluble and stable at room temperature
  - C. Water soluble and stable at room temperature
  - D. Water insoluble and unstable

Answer Key

- **Q1:** A - It is a colourless crystalline solid as per its physical description.
- **Q2:** C - It decomposes easily in dry state and is stable only when cold.
- **Q3:** B - Benzenediazonium fluoroborate is water insoluble and stable at room temperature.

Memory Aids

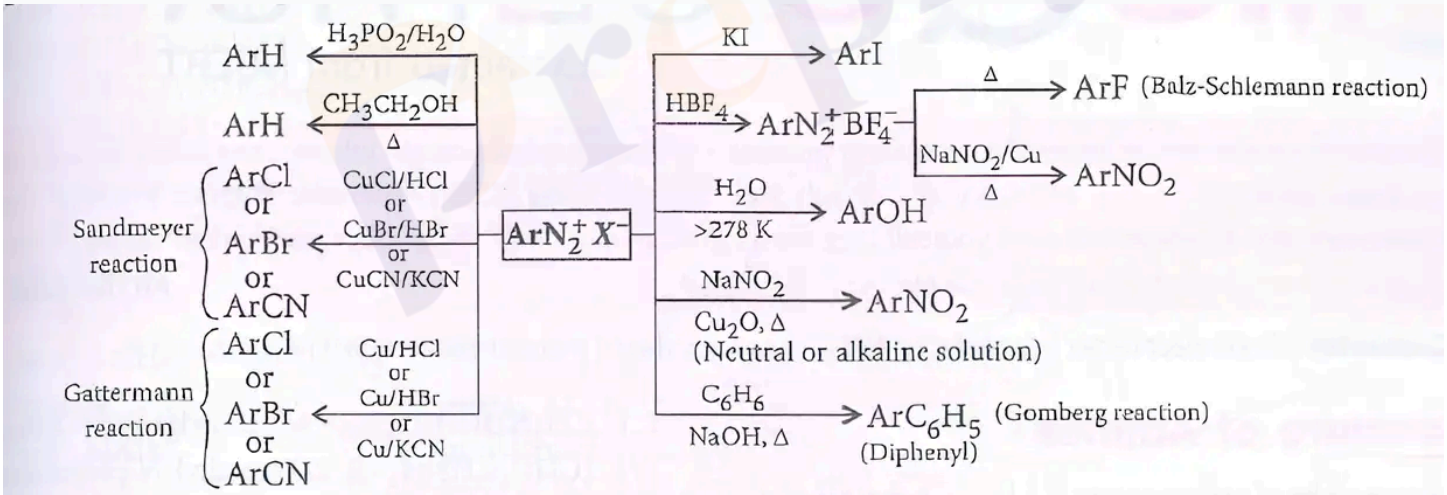
- Benzenediazonium chloride: "Cold stable, water soluble, dry state decomposes".

- Benzenediazonium fluoroborate: "Water insoluble, room temperature stable".

Reactions involving displacement of nitrogen (diazo group)

Explanation

- Arenediazonium salts ($ArN_2^+X^-$) are key intermediates in aromatic substitution.
- Displacement of N_2 group leads to various substituted aromatic compounds.
- Common reagents and products:
  - KI → ArI (aryl iodide)
  - HBF_4, heat (Δ) → ArF (aryl fluoride) via Balz-Schiemann reaction
  - H_2O, high temperature → ArOH (phenol)
  - $NaNO_2$, Cu → $ArNO_2$ (nitrobenzene)
  - NaOH, benzene (C_6H_6) → ArC_6H_5 (diphenyl) via Gomberg reaction
  - Sandmeyer and Gattermann reactions use Cu salts to form ArCl, ArBr, ArCN
  - Conversion back to ArH (aromatic hydrocarbon) is also possible.



Solved Examples

- **Ex 1:** Convert $ArN_2^+X^-$ to ArI using KI.
  - Step 1: Add KI to arenediazonium salt.
  - Step 2: $ArN_2^+X^- + KI \rightarrow ArI + N_2 + KX$
- **Ex 2:** Prepare ArF from arenediazonium salt.
  - Step 1: Treat $ArN_2^+X^-$ with HBF_4 and heat.
  - Step 2: $ArN_2^+X^- \rightarrow ArF + N_2 + BF_3$

Practice Set

- Q1: Which reagent converts $ArN_2^+X^-$ to ArI?
  - A. NaOH
  - B. KI
  - C. HBF_4
  - D. CuCl
- Q2: The Balz-Schiemann reaction produces:
  - A. ArCl
  - B. ArF
  - C. ArBr
  - D. ArCN
- Q3: Which reaction forms diphenyl (ArC_6H_5)?
  - A. Sandmeyer reaction
  - B. Gomberg reaction
  - C. Gattermann reaction
  - D. Balz-Schiemann reaction

Answer Key

- Q1: B - KI replaces diazo group with iodine forming ArI.
- Q2: B - Balz-Schiemann reaction converts diazonium salt to aryl fluoride (ArF).
- Q3: B - Gomberg reaction couples arenediazonium salt with benzene to form diphenyl.

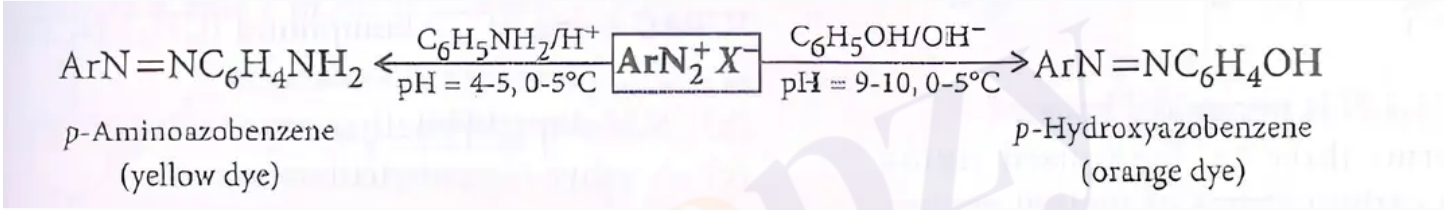
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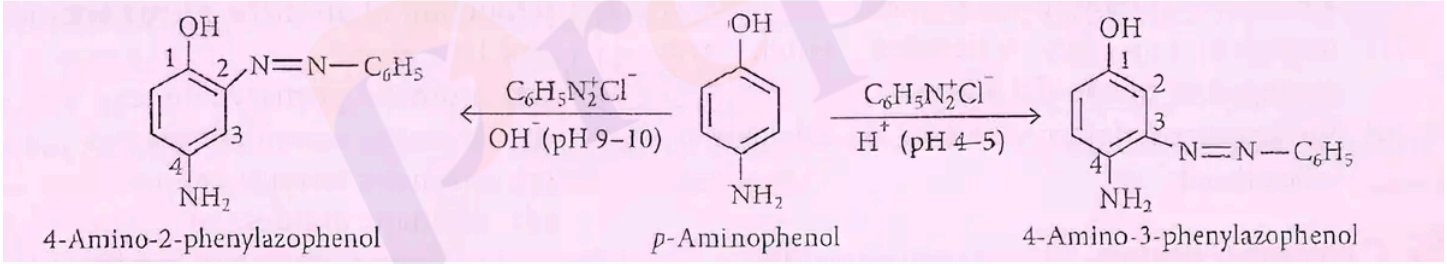
- "KI for Iodine" - KI replaces N_2^+ with I.
- Balz-Schiemann = ArF formation using HBF_4 and heat.
- Sandmeyer uses Cu salts for ArCl, ArBr, ArCN.
- Gomberg reaction forms diphenyl from ArN_2^+ and benzene.

Reactions involving retention of diazo group (coupling reactions)

Explanation

- Diazonium salts ($ArN_2^+X^-$) can couple with aromatic compounds retaining the diazo group.
- Coupling depends on pH and reagents, producing azo dyes.
- Example: p-aminoazobenzene forms diazonium salt intermediate at low temperature and acidic pH.
- Adding phenol under basic conditions (pH 9-10) forms p-hydroxyazobenzene (orange dye).
- In p-aminophenol, coupling position depends on pH:
  - Acidic (pH 4-5): coupling ortho to amino group.
  - Basic (pH 9-10): coupling ortho to phenolic group.





Solved Examples

- **Ex 1:** Formation of p-hydroxyazobenzene from p-aminoazobenzene.
  - Step 1: Diazotize p-aminoazobenzene with aniline and acid at 0-5°C, pH 4-5.
  - Step 2: Add phenol and base (OH^-) at pH 9-10, low temperature.
  - Step 3: Diazonium salt couples with phenol forming p-hydroxyazobenzene.
- **Ex 2:** p-Aminophenol coupling position changes with pH.
  - Acidic pH (4-5): Coupling ortho to $-NH_2$ group forming 4-amino-3-phenylazophenol.
  - Basic pH (9-10): Coupling ortho to -OH group forming 4-amino-2-phenylazophenol.

Practice Set

- Q1: What is the product when p-aminoazobenzene is diazotized and reacted with phenol at pH 9-10?
  - A. p-Aminoazobenzene
  - B. p-Hydroxyazobenzene
  - C. Phenol
  - D. Aniline
- Q2: In acidic medium, coupling of p-aminophenol occurs at which position?
  - A. Ortho to -OH
  - B. Ortho to $-NH_2$
  - C. Para to -OH
  - D. Para to $-NH_2$
- Q3: Which pH favors coupling ortho to phenolic group in p-aminophenol?
  - A. pH 4-5
  - B. pH 7
  - C. pH 9-10
  - D. pH 1-2

Answer Key

- Q1: B - Phenol reacts with diazonium salt at basic pH to form p-hydroxyazobenzene.
- Q2: B - Acidic medium causes coupling ortho to amino ($-NH_2$) group.
- Q3: C - Basic pH (9-10) favors coupling ortho to phenolic (-OH) group.

Memory Aids

- Coupling reactions retain diazo group forming azo dyes.
- Acidic pH → coupling near amino group.
- Basic pH → coupling near phenol group.
- p-Aminoazobenzene → diazotization → azo dye formation.